

Hyperpolarizability dispersion measured for Kr and Xe

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The frequency dependence of the second hyperpolarizabilities (γ) of Kr and Xe have been measured in the visible by means of gas phase electric-field-induced second-harmonic generation (ESHG). A simple model relating the dispersion of the nonresonant electronic contribution to γ for different third-order nonlinear optical processes is derived. This model is tested by comparing the results obtained here with those obtained by other methods.

INTRODUCTION

A large variety of nonlinear optical processes are mediated by the macroscopic third-order susceptibility $\chi^{(3)}$, which is ultimately determined by the second hyperpolarizability γ of the constituent atoms or molecules of the medium.¹⁻⁴ While the hyperpolarizabilities for the different nonlinear optical processes are all intimately related through a common quantum mechanical expression,^{2,5-7} in practice the combined effects of low measurement accuracy and widely differing experimental methods make it difficult to discern a pattern in the various experimental results for a given atom or molecule. However, there is a twofold motivation for attempting to understand the relationship between the various hyperpolarizabilities. First, the differences between the γ 's gives information on molecular electronic structure and vibrations.^{8,9} Second, nonresonant background susceptibilities have an important influence on the accuracy of measurements made to estimate population densities and transition frequencies by various forms of four wave mixing (FWM) spectroscopy.^{1,2,10} Note that the experiments whereby the nonresonant γ may be most accurately determined are not necessarily the same as the experiments for which the accurate value of γ is required.

Comparison of the hyperpolarizabilities for different processes should be simplest in the case of the inert gas atoms, where only the electronic degrees of freedom contribute to γ , and where the system is far below all resonances at the optical frequencies employed. Furthermore, for Kr and Xe the frequency dependence is expected to be strong enough to allow the different processes to be distinguished even with 10% error bars on the measurements. In what follows, we will first present a model from which one derives a simple relationship between the nonresonant electronic contributions to γ for all processes. Then the results of an electric-field-induced second-harmonic generation (ESHG) experiment will be given for Kr and Xe. Finally, these ex-

perimental results will be compared, within the context of the simple model, with results taken from the literature for other third-order optical processes.

THEORY

An explicit quantum-mechanical expression for γ , appropriate when damping may be ignored and suitable even in the static limit, has been derived by Orr and Ward.⁵ For a nondipolar molecule their result may be written as

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} K(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \times \sum_P \left\{ \sum_{\substack{m,n,p \\ (\neq g)}} \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|n\rangle \langle n|\mu_\gamma|p\rangle \langle p|\mu_\beta|g\rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1 - \omega_2)(\omega_{pg} - \omega_1)} - \sum_{\substack{m,n \\ (\neq g)}} \frac{\langle g|\mu_\alpha|m\rangle \langle m|\mu_\delta|g\rangle \langle g|\mu_\gamma|n\rangle \langle n|\mu_\beta|g\rangle}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_1)(\omega_{ng} + \omega_2)} \right\}, \quad (1)$$

where \sum_P denotes summation of the 24 terms generated by permuting the frequencies with their associated spatial subscripts, $-\omega_\sigma + \omega_1 + \omega_2 + \omega_3 = 0$, and μ_α is the α component of the electric dipole moment operator. The numerical coefficients $K(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$ are chosen such that γ for each process converges to the same value $\gamma(0; 0, 0, 0)$ in the static limit.^{2,5} While Eq. (1) is equivalent to the results obtained by other calculation schemes,^{6,7} its form is more convenient for the present purpose.

Taking Eq. (1) as the starting point, we make the following simplifying assumption. All the excited states of the system are assumed to be nearly degenerate, with the single effective resonance frequency of the system denoted by ω_0 . Such an assumption is most likely to be adequate when the optical frequencies are all much smaller than the transition frequencies of the system. Making this assumption, one may replace all transition frequencies ω_{mg} by ω_0 in Eq. (1), and the expression for the zzzz component of γ may then be factored to give

$$\gamma_{zzzz}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} K(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \times \left\{ \left[\sum_{\substack{m,n,p \\ (\neq g)}} \langle g|\mu_z|m\rangle \langle m|\mu_z|n\rangle \langle n|\mu_z|p\rangle \langle p|\mu_z|g\rangle \right] \sum_P [(\omega_0 - \omega_\sigma)(\omega_0 - \omega_1 - \omega_2)(\omega_0 - \omega_1)]^{-1} - \left[\sum_{\substack{m,n \\ (\neq g)}} \langle g|\mu_z|m\rangle \langle m|\mu_z|g\rangle \langle g|\mu_z|n\rangle \langle n|\mu_z|g\rangle \right] \sum_P [(\omega_0 - \omega_\sigma)(\omega_0 - \omega_1)(\omega_0 + \omega_2)]^{-1} \right\} = \hbar^{-3} K \{S_1 \cdot P_1 - S_2 \cdot P_2\}, \quad (2)$$

where S_1, S_2 are the two sums of products of matrix elements and P_1, P_2 are the corresponding sums of frequency-permuted resonance denominators. Explicitly evaluating P_1, P_2 and expanding in powers of ω/ω_0 , one obtains

$$\begin{aligned} \gamma_{zzzz}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) &= (\hbar\omega_0)^{-3} K(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \\ &\times \{S_1 [1 + \frac{1}{2}(\omega_L/\omega_0)^2 + \dots] \\ &- S_2 [1 + \frac{1}{2}(\omega_L/\omega_0)^2 + \dots]\}, \end{aligned} \quad (3)$$

where the effective laser frequency ω_L is defined by

$$\omega_L^2 \equiv \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2. \quad (4)$$

Finally,

$$\begin{aligned} \gamma_{zzzz}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) &= \gamma_{zzzz}(0; 0, 0, 0) \\ &\times [1 + C(\omega_L/\omega_0)^2 + \dots]. \end{aligned} \quad (5)$$

Our intention is to experimentally evaluate $\gamma_{zzzz}(0; 0, 0, 0)$ and $C\omega_0^{-2}$ for a given atom or molecule by means of dispersion measurements using a particular nonlinear optical process; γ for any other process is then determined by Eqs. (4) and (5). In the case of a molecule, Eq. (1) may be separated into terms which do or do not exhibit low frequency vibrational resonances. These are the vibrational or electronic contributions to γ , respectively.¹¹ Making this separation, Eq. (5) may be applied to describe the electronic part of the molecular hyperpolarizability. We will henceforth drop the spatial subscripts on γ since we will only be concerned with the $zzzz$ component in what follows. Discussion of the adequacy of the single resonance model will be deferred until later.

EXPERIMENT

The experimental technique has been described in detail elsewhere.¹¹⁻¹⁵ A cw laser beam from an argon-ion pumped dye laser, or from the argon-ion laser directly, is weakly focused through a sample cell containing the gas in which second-harmonic generation takes place. This is made possible by a symmetry breaking dc electric field. By arranging the electrodes so that the field direction alternates in direction every coherence length (adjusted by varying the gas density) periodic phase matching results, enhancing the second-harmonic signal generated. The electrode spacing is 2.69 mm resulting in optimal pressures in the range of 0.4–6 atm in the experiments reported here. A double prism spectrometer and glass filter serve to separate the second harmonic from the fundamental beam, and a photomultiplier tube is used to count signal photons.

The ratio of hyperpolarizabilities for a sample gas A and a reference gas B is obtained from the relation^{9,12}

TABLE I. Experimental results for γ_{Kr} and γ_{Xe} measured by ESHG. The uncertainty of the last digits is given in parentheses.

λ (nm)	γ_{Kr}/γ_{Ar}	γ_{Xe}/γ_{Ar}	γ_{Kr}^n ($10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$)	γ_{Xe}^n ($10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$)
650.0	2.359(6)	6.761(26)	2.024(10)	5.800(32)
590.0	2.402(11)	7.128(21)	2.153(13)	6.391(32)
514.5	2.477(7)	7.704(29)	2.397(12)	7.454(41)
488.0	2.502(7)	7.958(30)	2.506(12)	7.970(44)

* Obtained using Refs. 15 and 18.

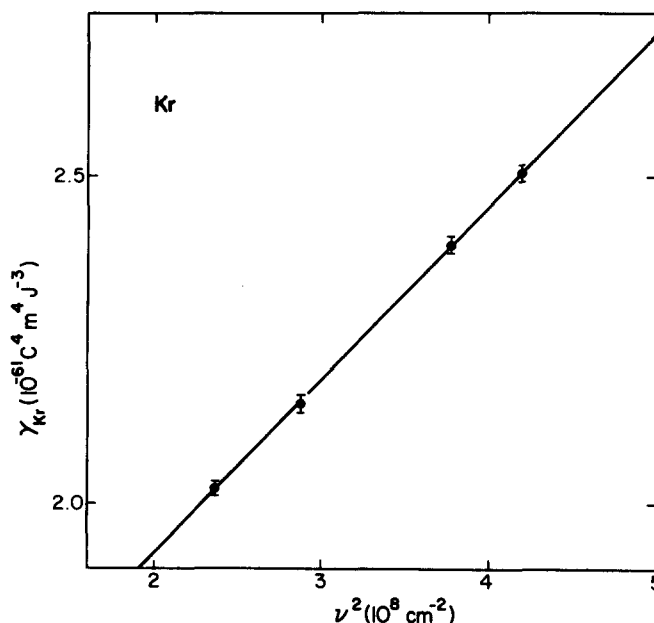


FIG. 1. Dispersion of the experimental results for γ_{Kr} measured by ESHG. The straight line is a least squares fit of the function $\gamma = A[1 + B\nu^2]$ to the data. The coefficients of the fit are $A = 1.397 \times 10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ and $B = 18.93 \times 10^{-10} \text{ cm}^2$, where ν is given in cm^{-1} .

$$\frac{\gamma_A}{\gamma_B} = \left[\frac{S_A^{(2\omega)}}{S_B^{(2\omega)}} \right]^{1/2} \left[\frac{\rho_A n_A}{\rho_B n_B} \right]^{-1}, \quad (6)$$

where $S^{(2\omega)}$ is the peak signal, ρ is the number density, and n is the refractive index of the gas at phase match, and in the present case $A = \text{Kr, Xe}$ and $B = \text{Ar}$. Since the optical and static field polarizations are parallel, the $zzzz$ component of γ is measured. The signals $S^{(2\omega)}$ were in the range 25–1000 cps, lower than usual because of the low breakdown voltage for the Ar reference gas. Sample densities were computed from the measured pressures and temperatures using the virial equation of state.¹⁶ Refractive indices were calculated from tables^{3,17} using the measured densities. High purity gases were used (min. 99.995%). The estimated total experimental uncertainty of a hyperpolarizability ratio measurement is obtained by convolving the statistical uncertainty for three runs with the uncertainty of the density determination due to the limited accuracy of the pressure gauge. The accuracy of the ratios is about $\pm 0.3\%$.

RESULTS AND DISCUSSION

The ratios γ_{Kr}/γ_{Ar} and γ_{Xe}/γ_{Ar} , measured at four wavelengths in this ESHG experiment, are given in Table I.

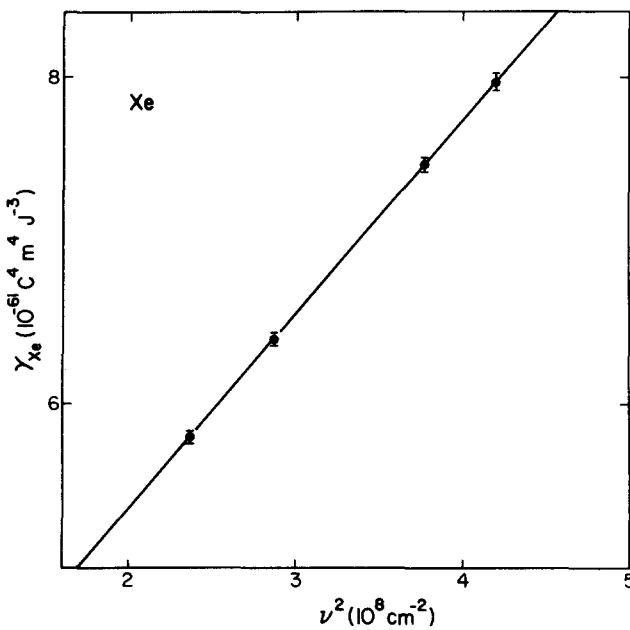


FIG. 2. Dispersion of the experimental results for γ_{Xe} measured by ESHG. The straight line is a least squares fit of the function $\gamma = A[1 + B\nu^2]$ to the data. The coefficients of the fit are $A = 2.999 \times 10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ and $B = 39.44 \times 10^{-10} \text{ cm}^2$, where ν is given in cm^{-1} .

In order to extract γ_{Kr} and γ_{Xe} from the ratios, use has been made of the previous measurements of γ_{Ar}/γ_{He} ,¹⁵ and the *ab initio* results of Sitz and Yaris for γ_{He} .¹⁸ Over the range of frequencies employed in the present measurements, the calibration results are adequately represented by¹⁵

$$\gamma_{Ar}/\gamma_{He} = 25.85[1 + (7.11 \times 10^{-10} \text{ cm}^2)\nu^2] \quad (7)$$

and¹⁹

$$\gamma_{He} = 42.6 \text{ a.u.}[1 + (2.94 \times 10^{-10} \text{ cm}^2)\nu^2], \quad (8)$$

where ν is given in cm^{-1} and $1 \text{ a.u.} = 6.2353 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. An uncertainty of $\pm 0.4\%$ due to the γ_{Ar}/γ_{He} calibration has been assumed in assigning error bars for γ_{Kr} and γ_{Xe} . The *ab initio* result for γ_{He} is thought to be accurate to 1%. No allowance has been made for the uncertainty of γ_{He} in arriving at the experimental results for γ_{Kr} and γ_{Xe} given in Table I.

TABLE II. Hyperpolarizabilities of Kr and Xe measured by several nonlinear optical processes.

Process	λ (nm)	γ_{Kr}^a ($10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$)	γ_{Xe}^a ($10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$)
dc Kerr ^b	632.8	1.71 ± 0.12	4.83 ± 0.39
FWM ^c	532,683	2.48 ± 0.35	...
ESHG ^d	694.3	2.16 ± 0.11	5.98 ± 0.42
THG ^e	694.3	2.87 ± 0.55	7.27 ± 1.38

^a Conversion factor $1 \text{ esu} = 6 \times 10^9/c^4 = 7.4279 \times 10^{-25} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ has been used, where the extra factor of 6 converts from susceptibility to hyperpolarizability.

^b $\gamma(-\omega; \omega, 0, 0)$, $\omega_L^2 = 2\omega^2$, from Ref. 19.

^c $\gamma(-2\omega_1 + \omega_2; \omega_1, \omega_1, -\omega_2)$, $\omega_L^2 = 4\omega_1^2 + 2(\omega_1 - \omega_2)^2$, from Ref. 10.

^d $\gamma(-2\omega; \omega, \omega, 0)$, $\omega_L^2 = 6\omega^2$, from Ref. 20.

^e $\gamma(-3\omega; \omega, \omega, \omega)$, $\omega_L^2 = 12\omega^2$, from Ref. 21.

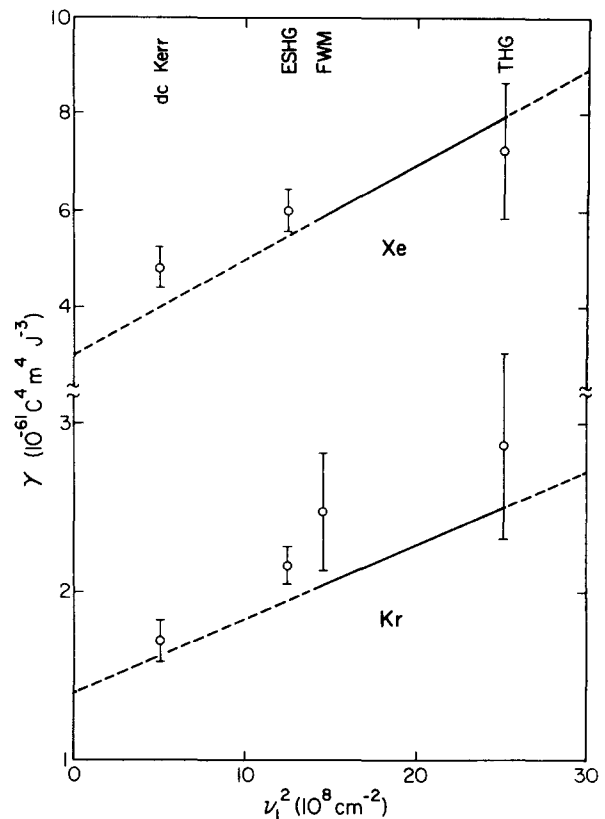


FIG. 3. Comparison of the hyperpolarizabilities of Kr and Xe measured by several nonlinear optical processes: dc Kerr effect, electric-field-induced second-harmonic generation (ESHG), four wave mixing (FWM), and third-harmonic generation (THG). The straight lines are the ESHG results shown in Figs. 1 and 2, replotted vs ν_L^2 . The effective laser frequency ν_L is defined by Eq. (4). The dashed portions of these lines indicate extrapolation outside the frequency interval containing the actual measurements. The open circles are the data of Table II. For each atom, all the results should fall on the same line if Eq. (5) accurately represents γ . Note the change of vertical scale at $\gamma = 3 \times 10^{-61}$.

The experimental ESHG results for γ_{Kr} and γ_{Xe} are very well represented by a function with the form of Eq. (5), as may be seen from the plots of γ_{Kr} and γ_{Xe} vs ν^2 in Figs. 1 and 2, respectively. The dispersion of γ is large, yielding an optical hyperpolarizability about twice as large as the static value (estimated by extrapolating the dispersion curve to $\nu = 0$). By making use of the ESHG data to fix all parameters in Eq. (5) for each atom, we may now address the question of whether the simple single resonance model accurately describes γ for the other nonlinear optical processes as well.

The values of γ obtained for Kr and Xe from dc Kerr,¹⁹ four wave mixing (FWM),¹⁰ ESHG,²⁰ and third-harmonic generation (THG)²² experiments are presented in Table II. In order to compare the hyperpolarizabilities for these processes we have plotted γ vs ν_L^2 in Fig. 3,²² where ν_L^2 is defined by Eq. (4) and where the appropriate frequency arguments for each process are given at the bottom of Table II. If Eq. (5) is an accurate description of γ , all the results for each atom should fall on a single straight line in Fig. 3. The results are in rough agreement with the prediction of Eq. (5), as may be seen from Fig. 3. This agreement favors Eq. (5), especially since measurements made by the different methods are for the most part quite independent (ESHG and THG are referenced to the *ab initio* γ_{He} , FWM is referenced to the N_2

Raman Q -branch intensity, while the dc Kerr measurements are self-contained). However, more accurate measurements are required, preferably over a range of wavelengths for each of several processes, if one is to experimentally test the single resonance model more strongly than at the 10%–20% level of accuracy.

There are several other lines of evidence in favor of our single resonance model. Equations (4) and (5) give the relative dispersion for dc Kerr, ESHG, and THG in the ratios 1:3:6. These ratios are the same as those obtained from an approximate calculation by a method due to Dawes²³ and subsequently extended by Finn.^{8,24} This calculation starts from Eq. (1) and also makes use of an effective resonance frequency, but does not assume near degeneracy of the transition frequencies. Furthermore, the *ab initio* calculation of Sitz and Yaris¹⁸ for γ_{He} also gives nearly the same dispersion ratios of 1:3.1:6.1 for dc Kerr: ESHG:THG. These results tend to indicate that the calculated relations between the various third-order nonlinear optical processes are not sensitive to the single resonance frequency assumption, notwithstanding the drastic appearance of that assumption.

If the relations expressed in Eq. (5) are in fact accurate, as suggested by the comparisons above, then ESHG measurements could be used to accurately calibrate the nonresonant electronic background seen in CARS measurements,^{1,2,10} after making allowance for the relatively small vibrational contributions.^{8–10} One could then reverse the usual procedure and calibrate Raman line cross sections in terms of the nonresonant background, with an overall accuracy comparable to that of the best direct determinations.²⁵ In this regard, improved *ab initio* results for γ_{He} would be desirable to provide a firm foundation for the calibration of ESHG measurements. We note that existing Kleinman symmetry measurements would provide an experimental test of such a calculation at the 0.1% level of accuracy.¹¹

Note added in proof: The recent, accurate THG measurements by H. J. Lehmeier *et al.* [Opt. Commun. **56**, 67 (1985)], give $\gamma_{\text{Kr}} = 1.74 \pm 0.17 \times 10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ and

$\gamma_{\text{Xe}} = 5.11 \pm 0.51 \times 10^{-61} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ at $\lambda = 1.055 \mu\text{m}$, in good agreement with the predicted dispersion curves in Fig. 3.

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- ¹Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984).
- ²M. D. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).
- ³M. P. Bogaard and B. J. Orr, in *International Review of Science, Physical Chemistry, Molecular Structure and Properties* edited by A. D. Buckingham (Butterworths, London, 1975), Ser. 2, Vol. 2, p. 149.
- ⁴D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer, Berlin, 1979).
- ⁵B. J. Orr and J. F. Ward, *Mol. Phys.* **20**, 513 (1971).
- ⁶N. Bloembergen, H. Lotem, and R. T. Lynch, *Ind. J. Pure Appl. Phys.* **16**, 151 (1978).
- ⁷Y. Prior, *IEEE J. Quant. Electron.* **20**, 37 (1984).
- ⁸D. S. Elliott and J. F. Ward, *Mol. Phys.* **51**, 45 (1984).
- ⁹D. P. Shelton and V. Mizrahi, *Chem. Phys. Lett.* (in press).
- ¹⁰T. Lundeen, S.-Y. Hou, and J. W. Nibler, *J. Chem. Phys.* **79**, 6301 (1983).
- ¹¹V. Mizrahi and D. P. Shelton, *Phys. Rev. A* **31**, 3145 (1985).
- ¹²D. P. Shelton and A. D. Buckingham, *Phys. Rev. A* **25**, 2787 (1982).
- ¹³D. P. Shelton, *Rev. Sci. Instrum.* **56**, 1474 (1985).
- ¹⁴V. Mizrahi and D. P. Shelton, *Phys. Rev. A* (in press).
- ¹⁵V. Mizrahi and D. P. Shelton, *Phys. Rev. Lett.* **55**, 696 (1985).
- ¹⁶J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon, Oxford, 1980).
- ¹⁷P. J. Leonard, *At. Data Nucl. Data Tables* **14**, 21 (1974).
- ¹⁸P. Sitz and R. Yaris, *J. Chem. Phys.* **49**, 3546 (1968).
- ¹⁹A. D. Buckingham and D. A. Dunmur, *Trans. Faraday Soc.* **64**, 1176 (1968).
- ²⁰R. S. Finn and J. F. Ward, *Phys. Rev. Lett.* **26**, 285 (1971).
- ²¹J. F. Ward and G. H. C. New, *Phys. Rev.* **185**, 57 (1969).
- ²²G. Rosasco (private communication).
- ²³E. L. Dawes, *Phys. Rev.* **169**, 47 (1968).
- ²⁴R. S. Finn, Ph.D. thesis, University of Michigan, Ann Arbor, 1971.
- ²⁵H. W. Klockner and H. W. Schrotter, in *Topics in Current Physics*, edited by A. Weber (Springer, Berlin, 1979).